Table III. Bond Distances (Å) for 1-Sn-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ and Their Estimated Standard Deviations

Sn(1)-C(2)	2.499 (5)	B(4)-B(5)	1.675 (9)
Sn(1)-C(3)	2.481 (6)	B(4)-B(7)	1.767 (9)
Sn(1)-B(4)	2.422 (6)	B(5)-B(6)	1.699 (9)
Sn(1)-B(5)	2.418 (8)	B(5)-B(7)	1.775 (9)
Sn(1)-B(6)	2.431 (7)	B(6)-B(7)	1.778 (9)
C(2)-C(3)	1.494 (7)	Si(1)-C(11)	1.862 (7)
C(2)-B(6)	1.582 (8)	Si(1)-C(12)	1.874 (7)
C(2)-B(7)	1.727 (8)	Si(1)-C(13)	1.870 (6)
C(2)-Si(2)	1.891 (4)	Si(2)-C(21)	1.859 (7)
C(3)-B(4)	1.583 (7)	Si(2)-C(22)	1.866 (9)
C(3)-B(7)	1.729 (9)	Si(2)-C(23)	1.868 (7)
C(3)-Si(1)	1.881 (5)		

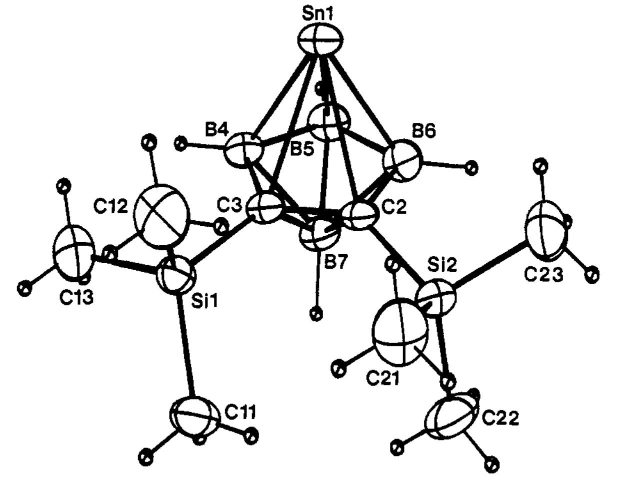

Figure 1. Molecular structure of *closo*-1-Sn-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (I) (ORTEP plot with 50% thermal ellipsoids).

BH units would become equivalent and hence would show a single resonance in its proton-decoupled boron-11 NMR spectrum. The significant upfield shift of the cage carbon resonance from those of the corresponding *closo*-stannacarborane precursor (I)[7] as well as the *nido*-2,3-dicarbahexaborane(8)[14] derivatives is consistent with the closo structure of II that is delocalized to some degree. The proton and the boron-11 NMR spectra and infrared spectra of II (see Experimental Section) are also consistent with those of the unsubstituted *closo*-1,2-dicarbahexaborane(6) reported by Shapiro and co-workers.[10]

Crystal Structure of the Stannacarborane Precursor *closo*-1-Sn-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ (I). The molecular structure of I (Figure 1, Tables III and IV) contains a distorted pentagonal-bipyramidal cluster core, SnC_2B_4, in which the Sn atom occupies a vertex site above the C_2B_3 plane and is "slipped" or displaced with respect to the centroid of this plane. The Sn-C distances [2.499 (5), 2.481 (6) Å] are longer than the Sn-B distances [2.422 (6), 2.418 (8), 2.431 (7) Å], suggesting weaker tin-carbon interaction than tin-boron interaction. B(7) occupies a vertex site below the C_2B_3 plane. Its distances to the C_2B_3 carbons [1.727 (8), 1.729 (9) Å] are shorter than the distances to the C_2B_3 boron atoms [1.767 (9), 1.775 (9), 1.778 (9) Å], which is consistent with the smaller radius of carbon than boron. The largest deviation from the least-squares plane defined by C_2B_3 is 0.017 Å for B(6). Distortions of the type observed in the structure of I have also been observed in other related main-group substituted carboranes: $Sn(Me_3Si)C_2B_4H_5$,[15] $Sn(Me_3Si)MeC_2B_4H_4$,[16] and 1-$MeGaC_2B_4H_6$.[17]

Table IV. Bond Angles (deg) for 1-Sn-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$ and Their Estimated Standard Deviations

C(2)-Sn((1)-C(3)	34.9 (2)	C(2)-C(3)-B(7)	64.3 (3)
C(2)-Sn(1)-B(4)	62.3 (2)	C(2)-C(3)-Si(1)	127.6 (3)
C(2)-Sn(1)-B(5)	64.6 (2)	B(4)-C(3)-B(7)	64.4 (4)
C(2)-Sn(1)-B(6)	37.5 (2)	B(4)-C(3)-Si(1)	120.4 (3)
C(3)-Sn(1)-B(4)	37.6 (2)	B(7)-C(3)-Si(1)	133.9 (4)
C(3)-Sn(1)-B(5)	64.5 (2)	Sn(1)-B(4)-C(3)	73.3 (3)
C(3)-Sn(1)-B(6)	62.3 (2)	Sn(1)-B(4)-B(5)	69.6 (3)
B(4)-Sn(1)-B(5)	40.5 (2)	Sn(1)-B(4)-B(7)	95.6 (3)
B(4)-Sn(1)-B(6)	66.3 (2)	C(3)-B(4)-B(5)	106.8 (4)
B(5)-Sn(1)-B(6)	41.0 (3)	C(3)-B(4)-B(7)	61.9 (3)
Sn(1)-C(2)-C(3)	71.9 (3)	B(5)-B(4)-B(7)	62.1 (4)
Sn(1)-C(2)-B(6)	69.0 (4)	Sn(1)-B(5)-B(4)	69.9 (3)
Sn(1)-C(2)-B(7)	94.0 (3)	Sn(1)-B(5)-B(6)	69.9 (3)
Sn(1)-C(2)-Si(2)	134.2 (2)	Sn(1)-B(5)-B(7)	95.5 (3)
C(3)-C(2)-B(6)	111.6 (4)	B(4)-B(5)-B(6)	103.8 (4)
C(3)-C(2)-B(7)	64.5 (3)	B(4)-B(5)-B(7)	61.5 (4)
C(3)-C(2)-Si(2)	132.4 (3)	B(6)-B(5)-B(7)	61.5 (3)
B(6)-C(2)-B(7)	64.8 (4)	Sn(1)-B(6)-C(2)	73.6 (3)
B(6)-C(2)-Si(2)	115.2 (3)	Sn(1)-B(6)-B(5)	69.1 (3)
B(7)-C(2)-Si(2)	130.3 (4)	Sn(1)-B(6)-B(7)	95.1 (3)
Sn(1)-C(3)-C(2)	73.1 (3)	C(2)-B(6)-B(5)	106.2 (4)
Sn(1)-C(3)-B(4)	69.2 (3)	C(2)-B(6)-B(7)	61.6 (3)
Sn(1)-C(3)-B(7)	94.5 (3)	B(5)-B(6)-B(7)	61.3 (3)
Sn(1)-C(3)-Si(1)	131.2 (3)	C(2)-B(7)-C(3)	51.2 (3)
C(2)-C(3)-B(4)	111.6 (4)	C(2)-B(7)-B(4)	93.5 (4)
C(2)-B(7)-B(5)	97.1 (4)	C(3)-Si(1)-C(13)	109.1 (2)
C(2)-B(7)-B(6)	53.6 (3)	C(11)-Si(1)-C(12)	113.0 (3)
C(3)-B(7)-B(4)	53.8 (3)	C(11)-Si(1)-C(13)	107.3 (3)
C(3)-B(7)-B(5)	96.6 (4)	C(12)-Si(1)-C(13)	107.8 (3)
C(3)-B(7)-B(6)	92.9 (4)	C(2)-Si(2)-C(21)	115.8 (3)
B(4)-B(7)-B(5)	56.5 (4)	C(2)-Si(2)-C(22)	108.5 (3)
B(4)-B(7)-B(6)	97.0 (4)	C(2)-Si(2)-C(23)	107.7 (3)
B(5)-B(7)-B(6)	57.1 (3)	C(21)-Si(2)-C(22)	110.1 (3)
C(3)-Si(1)-C(11)	111.8 (3)	C(21)-Si(2)-C(23)	105.7 (3)
C(3)-Si(1)-C(12)	107.8 (3)	C(22)-Si(2)-C(23)	108.7 (3)

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Supplementary Material Available: Listings of crystal data, bond distances, bond angles, positional parameters, and anisotropic thermal parameters (6 pages); a listing of calculated and observed structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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Contribution from the School of Chemistry,
University of Bath, Claverton Down,
Bath BA2 7AY, U.K., and Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Synthetic, Electrochemical, and Structural Studies of Monoalkyne Complexes of Molybdenum(II) and Tungsten(II)

Brian J. Brisdon,*[,1a] Annabelle G. W. Hodson,[1a]
Mary F. Mahon,[1a] Kieran C. Molloy,[1a]
and Richard A. Walton*[,1b]

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Introduction

There is a diversity of chemistry centered around d^4 metal complexes that contain an alkyne ligand acting as a 4-electron

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Table I. Product Yields, Elemental Microanalyses, and Selected Infrared Spectral Data for $MX_2(CO)(R'C_2R')(PR_3)_2$

complex	color	% yield	microanal, % found (calc) C	H	X	IR, cm^{-1} [a] ν(CO)	ν(C≡C)
$MoBr_2(CO)(MeC_2Me)(PEtPh_2)_2$	green	51	51.3 (51.7)	4.7 (4.7)	21.2 (20.9)	1955 s	1666 vw
$MoBr_2(CO)(MeC_2Me)(PEt_2Ph)_2$	green	44	44.4 (44.8)	5.4 (5.4)	23.9 (23.9)	1947 s	1670 vw
$MoCl_2(CO)(MeC_2Me)(PMePh_2)_2$	green	40	57.4 (57.3)	4.9 (4.9)	10.4 (10.9)	1939 s	1678 vw
$MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$	green	55	50.2 (50.4)	4.5 (4.3)	21.5 (21.7)	1951 s	1650 vw
$MoI_2(CO)(MeC_2Me)(PMePh_2)_2$	green	49	43.4 (44.7)	3.8 (3.8)		1921 s	1673 vw
$MoBr_2(CO)(MeC_2Me)(PMe_2Ph)_2$	green	40	41.2 (41.0)	4.7 (4.6)	26.2 (26.1)	1936 s	1677 vw
$WBr_2(CO)(MeC_2Me)(PMePh_2)_2$	purple	60	44.3 (45.0)	4.0 (3.9)	19.5 (19.4)	1901 s	1652 vw
$MoBr_2(CO)(PhC_2Ph)(PMePh_2)_2$	green	41	58.2 (57.1)	4.1 (4.2)		1980 s	1622 vw
$WBr_2(CO)(PhC_2Ph)(PMePh_2)_2$	purple	50	51.7 (51.8)	3.7 (3.8)		1953 s	1620 vw

[a] Nujol mulls.

Table II. Crystallographic Data for $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$

chem formula	$Br_2C_{31}H_{22}MoOP_2$	space group	*Pbca* (No. 61)
a, Å	31.569 (7)	T, °C	20
b, Å	12.701 (3)	λ (Mo Kα), Å	0.71069
c, Å	15.477 (7)	ρ_{calcd}, g cm^{-3}	1.56
V, Å^3	6205.36	μ(Mo Kα), cm^{-1}	30.1
Z	8	R^a	0.0635
fw	728.2	R_w^b	0.0639

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 3.0065/[\sigma^2(F_o) + 0.0010(F_o)^2]$.

Table III. Atomic Coordinates (×10^4) for the Most Significant Atoms of $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ and Their Estimated Standard Deviations[a]

atom	x	y	z	U_{eq}, Å^2
Mo(1)	1296.4 (5)	476.8 (11)	1541.3 (11)	432 (9)
Br(1)	1784.3 (6)	−1120.2 (15)	1993.1 (14)	644 (14)
Br(2)	1246.8 (7)	927.6 (17)	3246.8 (14)	726 (15)
P(1)	1970.9 (1)	1591.8 (4)	1586.7 (3)	497 (3)
P(2)	694.7 (1)	−814.3 (3)	1856.7 (3)	448 (3)
O(1)	1463.5 (4)	−419.4 (12)	−300.1 (10)	751 (11)
O(27)	1413.1 (6)	−95.6 (13)	414.5 (17)	590 (15)
C(28)	1010.7 (5)	1404.3 (12)	639.6 (14)	441 (12)
C(29)	906.2 (5)	1717.5 (14)	1453.9 (15)	545 (13)
C(30)	941.0 (7)	1676.9 (17)	−290.9 (14)	778 (17)
C(31)	677.2 (6)	2548.6 (16)	1892.7 (14)	740 (15)

[a] Data for the carbon atoms of the phosphine ligands are included in the supplementary material.

Table IV. Important Bond Distances (Å) and Bond Angles (deg) for $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$[a]

	Distances		
Mo–Br(1)	2.641 (2)	Mo–C(29)	2.005 (17)
Mo–Br(2)	2.705 (3)	C(27)–O(1)	1.191 (22)
Mo–P(1)	2.558 (5)	C(28)–C(30)	1.498 (27)
Mo–P(2)	2.556 (5)	C(28)–C(29)	1.362 (25)
Mo–C(27)	1.925 (25)	C(29)–C(30)	1.448 (26)
Mo–C(28)	2.037 (17)		
	Angles		
Br(1)–Mo–Br(2)	86.4 (1)	Br(1)–Mo–C(29)	168.5 (6)
P(1)–Mo–Br(1)	86.1 (1)	Br(2)–Mo–C(29)	82.2 (7)
P(1)–Mo–Br(2)	84.5 (1)	P(1)–Mo–C(29)	94.5 (5)
P(2)–Mo–Br(1)	83.7 (1)	P(2)–Mo–C(29)	93.5 (5)
P(2)–Mo–Br(2)	84.6 (1)	C(27)–Mo–C(29)	110.7 (8)
P(2)–Mo–P(1)	165.5 (2)	C(28)–Mo–C(29)	39.4 (7)
Br(1)–Mo–C(27)	80.7 (5)	Br(2)–Mo–C(28)	121.4 (6)
Br(2)–Mo–C(27)	167.1 (5)	C(29)–C(28)–Mo	69.0 (11)
P(1)–Mo–C(27)	94.3 (6)	C(30)–C(28)–Mo	149.1 (15)
P(2)–Mo–C(27)	94.2 (5)	C(30)–C(28)–C(29)	141.9 (16)
Br(1)–Mo–C(28)	152.1 (6)	C(28)–C(29)–Mo	71.6 (11)
P(1)–Mo–C(28)	93.9 (5)	C(31)–C(29)–Mo	148.0 (18)
P(2)–Mo–C(28)	99.9 (5)	C(31)–C(29)–C(28)	140.1 (19)
C(27)–Mo–C(28)	71.5 (8)	Mo–C(27)–O(1)	176.0 (17)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

donor.[2-6] Thus, reductive coupling of CO ligands on a Ta(I) center is facilitated by the stabilities of the resultant monoalkyne complexes.[3] Reaction of nucleophiles with alkyne ligands in the cationic species $\{Mo(\eta^5\text{-}C_5H_5)(\eta^2\text{-}RC_2R')[P(OMe)_3]_2\}BF_4$ leads to η^2-vinyl or η^3-alkenyl derivatives,[4,5] and the conversion from a d^6 metal–alkyne complex to a d^4 alkoxoalkyne complex combines electrophilic addition at the ligand β-position with known carbyne–carbonyl coupling.[6] It is surprising therefore that the divergent influences of ligand π-acceptance and π-donation on the frontier orbitals of d^4 metal complexes containing a 4-electron-donor alkyne ligand have been probed by electronic spectral and cyclic voltammetric studies on just one series of pseudooctahedral complexes.[7] In part, this can be traced to the lack of synthetic methods suitable for preparing series of related complexes containing this ligand. In this report we describe a general route to complexes of the type $MX_2(CO)(R'C_2R')(PR_3)_2$ (M = Mo or W; X = Cl, Br, or I). The crystal and molecular structure of one of these derivatives, namely $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$, has also been determined.

Experimental Section

Starting Materials. The complexes of the type $MX_2(CO)_2(PR_3)_2(NCMe)$ were prepared by the use of the literature method.[8] All phosphine and alkyne ligands and solvents were obtained from commercial sources. Solvents were dried and distilled prior to use.

Synthesis of $MX_2(CO)(R'C_2R')(PR_3)_2$. Complexes of this type (M = Mo, R' = Me, X = Br, and PR_3 = $PEtPh_2$, PEt_2Ph, $PMePh_2$, or PMe_2Ph; M = Mo, X = Cl or I, and PR_3 = $PMePh_2$; M = Mo or W, R' = Ph, X = Br, and PR_3 = $PMePh_2$; M = W, R' = Me, X = Br, and PR_3 = $PMePh_2$) were prepared by the same general method. An excess of 2-butyne or diphenylacetylene (10 mmol) was dissolved in dry CH_2Cl_2 (15 mL), and the solution was added under an atmosphere of N_2 gas to a freshly prepared solid sample of $MoX_2(CO)_2(PR_3)_2(NCMe)$ (0.5 mmol). The resulting mixture was stirred at room temperature for 12 h (M = Mo) or at 40 °C for 8 h (M = W). The filtered solution was then concentrated in vacuo and n-hexane (5 mL) added. Refrigeration of this solution yielded the product as fine green or purple needles, which were recrystallized from CH_2Cl_2/hexane. Product yields, elemental microanalyses, and selected infrared spectral data are given in Table I.

Preparation of Single Crystals of $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$. A sample of $MoBr_2(CO)(MeC_2Me)(PMePh)_2$ was recrystallized twice from a CH_2Cl_2/hexane mixture at −10 °C to produce crystals suitable for an X-ray single-crystal structure determination. A cubic crystal of approximate dimensions 0.2 × 0.2 × 0.2 mm was selected from this batch and used for data collection.

X-ray Crystallography. The structure of $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ was determined by the application of standard procedures. The basic crystallographic procedures are listed in Table II. Three standard reflections were measured after every 5000 s of beam time

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(1) (a) University of Bath. (b) Purdue University.

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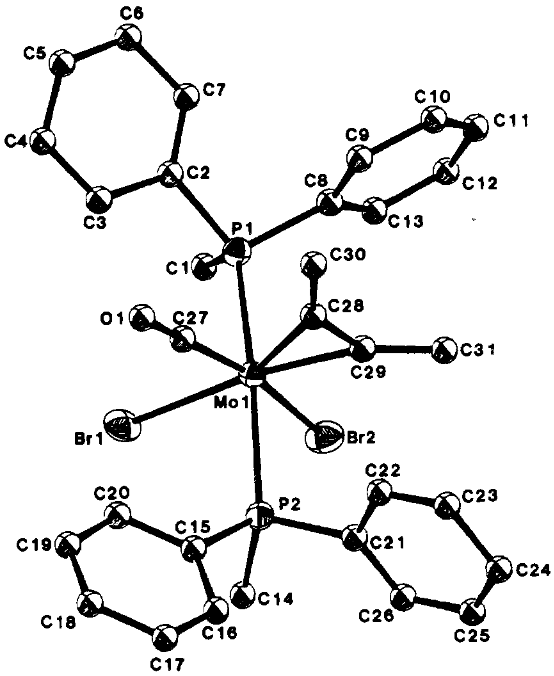

Figure 1. ORTEP representation of the structure of $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ showing the atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level for all atoms except the methyl group and phenyl ring carbon atoms of the phosphine ligands. The latter atoms are represented as spheres of arbitrary radius.

during data collection; there was no systematic variation in intensity. Data were measured at room temperature on a Hilger and Watts Y290 automatic four-circle diffractometer in the range $4 < 2\theta < 44°$. From a set of 4348 reflections collected, 3098 were unique and 1790 had $I \geq 3\sigma I$. Data were corrected for Lorentz and polarization effects but not for extinction or absorption. The structure was solved by conventional Patterson methods and refined by using the SHELX[9,10] suite of programs. In the final least-squares cycles the Mo(1), Br(1), Br(2), P(1), P(2), O(1), C(27), C(28), C(29), C(30), and C(31) atoms were refined anisotropically; all other atoms, isotropically. Hydrogen atoms were not included. Final residuals after 13 cycles of full-matrix least-squares refinement were $R = 0.0635$ and $R_w = 0.0639$ for a weighting scheme of $w = 3.0065/[\sigma^2(F_o) + 0.0010(F_o)^2]$. The largest peak in the final difference Fourier map was 0.29 e/Å^3 and was not of any chemical significance. Scattering factors and anomalous dispersion corrections were obtained from ref 11.

Atomic coordinates and their errors for the most significant atoms are listed in Table III. Important intramolecular bond distances and angles are given in Table IV. The asymmetric unit is shown in Figure 1 along with the full atomic labeling scheme used. Tables giving full details of the crystal data and data collection parameters (Table S1), the atomic coordinates for all atoms (Table S2), the anisotropic thermal parameters (Table S3), and complete bond distances (Table S4) and bond angles (Table S5) are available as supplementary material.

Physical Measurements. Infrared spectra were recorded as Nujol mulls with the use of a Perkin-Elmer 599B spectrometer, while ^1H and ^{13}C NMR spectra were obtained on CD_2Cl_2 solutions of the complexes on a JEOL GX 270-MHz spectrometer with TMS as an internal reference. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{p,a}$ and $E_{p,c}$ values were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple, which was used as an internal standard.

Results

The monoalkyne complexes of Mo(II) and W(II) that are the subject of the present report were prepared by the procedure shown in eq 1. These complexes were characterized on the basis of their

$$MX_2(CO)_2(PR_3)_2(NCMe) + R'C_2R' \xrightarrow{CH_2Cl_2} MX_2(CO)(R'C_2R')(PR_3)_2 + CO + NCMe \quad (1)$$

IR and NMR spectral properties and by cyclic voltammetry, the details of which are presented in Tables I and Tables S6–S8 (supplementary material). The complex $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ has been structurally characterized by X-ray crystallography, the results of which are given in Tables II–IV and in Figure 1.

Discussion

A limited number of monoalkyne complexes of Mo(II) and W(II) of general formula $MX_2(CO)(R'C_2R')(PR_3)_2$ (M = Mo or W; R′ = alkyl or aryl; X = halogen) have been prepared previously from $MX_2(CO)_n(PR_3)_2$ [n = 2 or 3; $PR_3 = PPh_3$, PEt_3, or $^1/_2$ $Ph_2PCH_2CH_2PPh_2$] by direct reaction with excess alkyne at elevated temperatures and reaction times of up to 6 days.[12] This method has to date been successfully employed only where loss of CO from the parent tricarbonyl complex leads to a relatively stable six-coordinate dicarbonyl monomer $MX_2(CO)_2(PR_3)_2$, and since few such monomers are known, the method is not of general applicability. However, since there are many examples in molybdenum and tungsten chemistry of the facile displacement of weakly bonded nitrile ligands,[13] we have used the intermediacy of $MX_2(CO)_2(PR_3)_2(NCMe)$ complexes to provide a general route to the alkyne derivatives $MX_2(CO)(R'C_2R')(PR_3)_2$ (Table I). The relative rate of alkyne complex formation from $MX_2(CO)_2(PR_3)_2(NCMe)$ shows no strong halogen or phosphine dependency for a given metal, and thus the previously unobtainable $PMePh_2$ (X = Br or Cl) and PMe_2Ph (X = Br) complexes, as well as stable iodo–alkyne analogues, can be obtained with equal facility. The only previously known member of this class of iodo–alkyne complex is $MoI_2(CO)(R'C_2R')(PPh_3)_2$,[14] which was obtained by a circuitous route involving initial reaction of the alkyne with $MoI_2(CO)_3(NCMe)_2$ to form the unstable intermediate $MoI_2(CO)(R'C_2R')(NCMe)_2$, which rapidly dimerizes to unstable $[Mo(\mu\text{-}I)I(CO)(R'C_2R')(NCMe)]_2$ and can then be cleaved by PPh_3 to yield the pseudooctahedral monomeric product. A few closely related tungsten(II) derivatives of stoichiometry $WI_2(CO)_2(RC_2R')(L)$ (R = R′ = H and R = H when R′ = Ph; L = PMe_3, $AsMe_3$, *t*-BuNC) have also been reported; their preparation involves the reaction of $WI_2(CO)_4(L)$ with RC_2R'.[15]

Spectroscopic and Electrochemical Data. Selected infrared spectral data for the complexes are given in Table I. A strong, single carbonyl stretching frequency in the range 1901–1955 cm^{-1} characterizes these monocarbonyls, and a very weak absorption between 1620 and 1678 cm^{-1} is attributed to the $\nu(C\equiv C)$ stretching mode; these values show a decrease of 600 cm^{-1} or so from the uncoordinated alkyne, indicating considerable reduction of the C—C bond order, in keeping with the alkyne acting as a 4-electron donor. The room-temperature ^1H NMR spectral data for the $MX_2(CO)(R'C_2R')(PR_3)_2$ complexes show multiplets between δ +7.6 and δ +7.0 for the aromatic substituents of the alkyne and phosphine ligands. The alkyne methyl protons of the 2-butyne complexes produce a signal between δ +2.4 and δ +2.3, which is in most cases resolvable into a triplet due to coupling with two equivalent phosphorus nuclei (J_{P-H} = 1.5 Hz). ^{13}C NMR resonances are observed between δ +128 and δ +138 for aromatic phosphine and alkyne substituents, and the alkyne carbon atoms resonate as triplets centered between δ +225 and δ +230 with $^2J_{P-C}$ = 5.5–5.9 Hz. These latter values are typical of a cis P—M—C geometry, and the chemical shift data are as expected for 4-

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electron-donor alkynes.[7] Further details of the NMR spectral data are available as supplementary material (Tables S6 and S7).

The electrochemical properties of this group of complexes as measured by the cyclic voltammetric (CV) technique on solutions in 0.1 M n-Bu_4NPF_6/CH_2Cl_2 are very similar. In no instances were any of the redox processes reversible on the CV time scale (see Table S8). Two well-defined oxidations are observed for each of the complexes ($E_{p,a}(1) \simeq +1.0$ V and $E_{p,a}(2) \simeq +1.45$ V vs Ag/AgCl), but for neither of these processes is there a coupled reduction wave signifying reversal of these oxidation steps. These oxidations, which are listed in Table S8, did not vary greatly between the different complexes. In the series $MoX_2(CO)(MeC_2Me)(PMePh_2)_2$, the processes undergo small shifts to more positive potentials in the order Cl < Br < I (e.g. $E_{p,a}(1) = +0.94$, +1.03, and +1.04 V for X = Cl, Br, and I, respectively). Each of the complexes also displayed an irreversible reduction in the potential range $E_{p,c} = -1.0$ to -1.6 V (Table S8). These CV properties resemble those reported previously by Templeton and co-workers[12] for solutions of the related complexes $MoX_2(CO)(MeC_2Me)(PEt_3)_2$ (X = Cl or Br), $MoCl_2(CO)(MeC_2Me)(PPh_3)_2$, and $MoBr_2(CO)(PhC_2H)(PEt_3)_2$ in 0.1 M n-Bu_4NClO_4/CH_3CN, in which the onset of the first oxidation was around +0.9 V and there was a reduction wave between −1.0 and −1.2 V vs SSCE.

Structure of $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$. The close relationship of the complexes prepared in the present study and those reported previously by Templeton and co-workers[12] is clearly established from the preceding spectroscopic and electrochemical characterization. Further confirmation is provided by a single-crystal X-ray structure determination of $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$. Figure 1 shows an ORTEP view of the molecule and the atomic numbering scheme used. Key structural parameters are given in Table IV. The central molybdenum atom can be described as heptacoordinate, being bonded to two bromines [Mo–Br(1) = 2.641 (2), Mo–Br(2) = 2.705 (3) Å], one carbonyl carbon [Mo–C(27) = 1.93 (3) Å], two phosphine groups [Mo–P(1) = 2.558 (5), Mo–P(2) = 2.556 (5) Å], and a bidentate 2-butyne ligand [Mo–C(28) = 2.04 (2), Mo–C(29) = 2.01 (2) Å]. A pair of cis bromide ligands and the carbonyl and alkyne groups occupy the girdle plane of the pentagonal-bipyramidal arrangement, with the phosphine ligands mutually trans in axial positions. Although there is no crystallographic symmetry imposed on the molecule, the structure has virtual C_s symmetry, with the mirror plane defined by Mo, Br(1), Br(2), C(27), and the entire alkyne unit.

Bond lengths between the metal atom and the phosphine groups and bromides are not significantly different from those observed for other molybdenum(II) halocarbonyl phosphine complexes.[12,16] The alkyne carbon–carbon bond length [C(28)–C(29) = 1.36 (3) Å] has been shown in general not to be much affected by the nature of the substituents or degree of electron donation to the metal.[17] The bent cis alkyne geometry has been observed previously in 2-butyne complexes and the metal–alkyne carbon distances have been shown to reflect the extent of electron donation to the metal.[17,18] For molybdenum or tungsten d^4 monocarbonyl alkyne derivatives, 2-, 3-, or 4-electron donation has been characterized by typical average M–C bond lengths of 2.10, 2.06, and 2.00 Å, respectively, and thus the average Mo–C(alkyne) distance of 2.02 Å in $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ is in keeping with 4-electron donation from the butyne group.

The parallel configuration of the carbonyl and alkyne groups in the *cis*-Mo(CO)(alkyne) unit also occurs in the related complexes $MoBr_2(CO)(PhC_2H)(PEt_3)_2$[12] and $W(CO)(HC_2H)(S_2CNEt_2)_2$[17] and arises from optimization of the π-donor and π-acceptor capabilities of the alkyne. The relatively short carbonyl–alkyne carbon–carbon distance [C(27)–C(28)] of 2.32 (1) Å in $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ is consistent with a weak 3-center, 2-electron interaction,[12] in which the metal d_{xz} orbital is stabilized by mixing of the CO π^* and alkyne π^* orbitals, and can be compared with an even shorter analogous carbon–carbon distance of 2.29 (1) Å in $MoBr_2(CO)(PhC_2H)(PEt_3)_2$.[12]

A pentagonal-bipyramidal (PB) structure is predicted for molecules of the type M(unidentate)$_5$(bidentate) that contain chelates with normalized bites of less than 1.1.[19] In $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$, the bite of the 2-butyne unit falls well below this value at 0.72 and, as expected, the alkyne occupies adjacent sites in the girdle. Distortion within the PB environment is evident from the bond distances around the girdle and from the position of the axial phosphorus atoms, which are at an angle of 165.5° and are bent toward the two bromine atoms. However, calculation of the dihedral angles between the L_{eq}–L_{ax}–L_{eq} planes and the L_{ax}–M–L_{eq} angles (L_{ax} = axial ligand, L_{eq} = equatorial ligand) gives average values of 57.2 and 91.0°, respectively, not dissimilar from the values of 54.4 and 90° for the ideal PB geometry.

In their discussion and prediction of electronic site preferences of donor and acceptor ligands in seven-coordinate d^4 species, Hoffmann et al.[20] considered only those combinations of ligands whose π-donating or π-accepting abilities were clearly distinguished and predicted an order of site preference of axial > equatorial for acceptor ligands in d^4 complexes with PB geometry. For $MoBr_2(CO)(MeC_2Me)(PMePh_2)_2$ and $MoBr_2(CO)(PhC_2H)(PEt_3)_2$,[12] the strongest π-acceptor is the carbonyl ligand, which is found in the girdle plane and not in a predicted axial site. However, if the 4-electron-donor characteristics of the alkyne ligands are taken to imply a metallacyclopropene formalism, then the formal oxidation state of the metal can be considered as M(IV). In this event, these will be d^2 complexes and the site preference arguments will be no longer valid. In any case, it may be that the steric effects of the phosphines and the M–alkyne chelate ring determine both the overall geometry and the specific location of substituent atoms.

Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), atomic coordinates (Table S2), thermal parameters (Table S3), bond distances (Table S4), bond angles (Table S5), NMR spectral data (Tables S6 and S7), and cyclic voltammetric data (Table S8) (12 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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